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Growth, structural, vibrational, optical, mechanical studies of Boric acid doped KAP single crystal

V. Thendral[1], P. Suganthi[1], G. Marudhu[2]*, A. Thayumanavan[1], G. Pasupathi[1], S. Krishnan[3], M. Prabhaharan[2]

[1]Department of Physics, A.V.V.M Sri Pushpam College, Poondi-613503, India
[2]Department of Physics, Aksheyaa College of Eng., Madhuranthagam - 603 314, India
[3]Department of Physics, Ramakrishna Mission Vivekananda College, Chennai - 600 004, India

Abstract : The growth and characterization of boric acid doped potassium acid phthalate (KAP) single crystals grown from low temperature solution growth method. The cell parameters were determined by single crystal X-ray diffraction analysis. The presence of various functional groups of boron doped KAP is confirmed by FTIR. The UV-Vis-NIR spectrum reveals the high percentage of transmission of the sample in the entire visible region. The DSC curve indicates that the crystal is structurally stable upto 299°C. Microhardness investigations are conducted on the grown crystals. The SHG of boric acid doped KAP is confirmed by Kurtz powder technique.

1. Introduction

Modern technologies based on optoelectronics, acousto-optics, have exploited the versatile properties of crystals. The development of the crystalline materials is the backbone of the modern technologies. Nonlinear optical (NLO) materials capable of efficient frequency conversion of visible and infrared wavelength are of great interest for applications in telecommunications, optical pumping, optical information processing etc. The fast development in the field of opto-electronics has stimulated the search for new nonlinear optical crystals for efficient signal processing. New nonlinear optical (NLO) frequency conversion materials can have a significant impact on laser technology, optical communication and data storage technology [1].

During last several years, search is concentrated on semi-organic materials due to their large nonlinearity, high resistance to laser induced damage and good mechanical hardness. One such semiorganic material is Potassium Acid Phthalate (KAP) ($C_8H_5KO_4$), crystals are used as the second, third and fourth harmonic generators for ND:YAG and ND: YLF lasers. The crystals are widely used for electro-optical applications as Q-switches for ND: YAG, ND: YLF, TI; sapphire and Alexandrite lasers, as well as for acoustic-optical applications. Many methods have been tried to increase the growth rate and improve the NLO properties of the KAP crystal. The addition of dopants and their influence on the growth process and properties

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of the crystals have been tried in recent years. The influence of alkali, alkaline earth and transition metals doping on the properties and crystalline perfection of KAP crystals[2]. Accommodating capability of ADP crystals with dopants like KCl and Oxalic acid reveals some interesting features [3]. Influence of Mn (II) doping on the NLO properties of ZTS reveals a good correlation of SHG efficiency and the crystalline perfection [4].Os (VIII)and Zn (II) doping effects on the properties and crystalline perfection of potassium hydrogen phthalate crystals [5,6].

It is already well-established borate family crystals have a good power threshold figure of merit and have a proven track record of enhancing the nonlinear optical nature of crystals. Novel metalorganic nonlinear optical materials like DipotassiumBoroMaleate (DKBM), Potassium Boro-Succinate (KBS), Cesium Triborate, CsB_3O_5 (CBO), Cesium Lithium Borate (CLBO), Strontium Boron Beryllium Oxide (SBBO), and Potassium Aluminum Borate (KABO) have been synthesized and investigated[7-12].Enhancement of properties of KDP and ADP by boron doping [13-14] has been studied. Thermal, microscopic, X-ray and spectral analyses are very important methods in materials characterization. Therefore, many authors have applied these techniques for various materials characterization [15-16]. In the light of research work being done on KAP crystals, to improve the properties, the present work focuses on boric acid as a dopant in KAP and this is expected to enhance the nonlinearity of the crystal. We have studied and reported the spectral, optical and mechanical behavior of boric acid doped KAP (BKAP) crystals.

2. Experimental

2.1 Synthesis and solubility

Boric acid doped Potassium Acid Phthalate was synthesized by adding 1 mole% Boric Acid (AR grade) with KAP in distilled water. The synthesized salt was purified by successive recrystallization process. As a first step towards crystallization of boric acid doped KAP, its solubility studies in water were carried out at different temperature (30-50˚C) .the solution of boric acid doped KAP was maintained at a constant temperature and continuously stirred using a magnetic stirrer to ensure homogeneous temperature and concentration, throughout the volume of the solution. On reaching saturation, the content of the solution was analyzed gravimetrically and this process was repeated for different temperatures. The solubility curve is shown in Figure.1. The solubility curve shows that boric acid doped KAP (BKAP) has positive solubility-temperature gradient and solution growth technique can be followed for crystal growth.

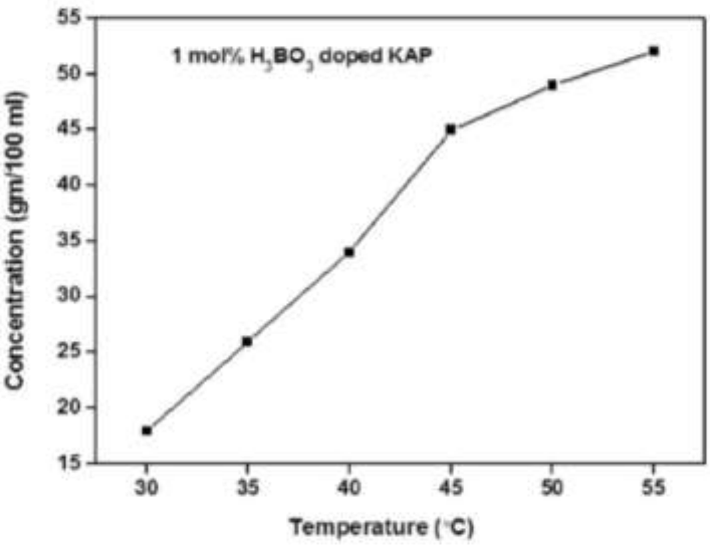

Fig. 1:Solubility curve of Boric acid doped KAP

2.2Crystal growth

Single crystals of boric acid doped Potassium Acid Phthalate were grown by slow evaporation solution growth at room temperature. The supersaturated solution of 1 mole% boric acid with KAP was prepared and kept in a vibrational free atmosphere. After a growth period of three weeks colorless, transparent and good quality crystals are obtained and are depicted in Fig.2.

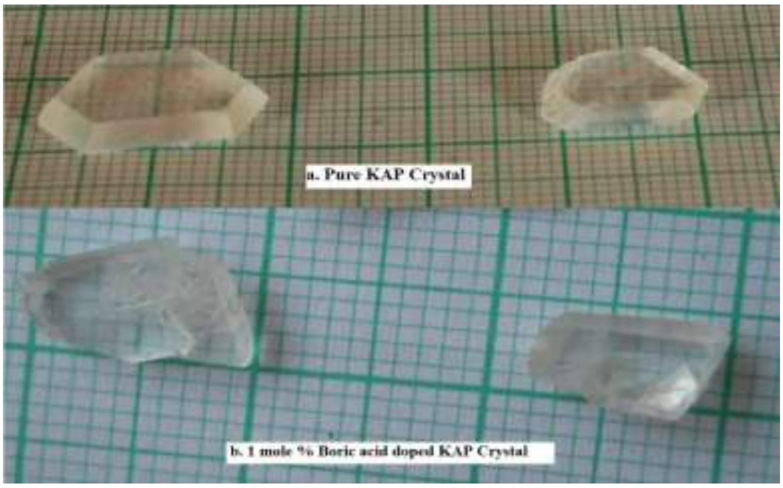

Fig.2: Crystal Images of a. pure KAP, b. Boric acid doped KAP

3. Results and discussion

3.1 Single crystal X-ray diffraction

Single crystal X-ray diffraction studies were performed on grown crystals to identify the structural parameters and degree of crystal perfection. From the collected data, it is observed that from the cell parameters of both pure KAP and boric acid doped KAP (BKAP) belong to orthorhombic crystal structure. The lattice parameters values of pure KAP are a = 9.605 Å, b = 13.331 Å, c = 6.473 Å, $\alpha = \beta = \gamma = 90^{\circ}$ and volume = 858.921 $Å^3$. The lattice parameters values of boric acid doped KAP are a = 9.69 ± 0.03Å, b = 13.39 ± 0.04 Å, c = 6.52 ± 0.02 Å, $\alpha = \beta = \gamma = 90^{\circ}$ and volume = 843 $Å^3$. The structural data of pure KAP and BKAP crystals are presented in Table 1.

Table.1: Unit cell parameter values of pure KAP and BKAP

Sample	Lattice parameters			Cell volume ($Å^3$)	$\alpha = \beta = \gamma$	Structure
	a(Å)	b(Å)	c(Å)			
Pure KAP	9.61	13.33	6.47	859	90°	Orthorhombic
1mole% boric acid + KAP	9.69	13.39	6.52	843	90°	Orthorhombic

3.2. FT-IR Spectral studies

The FTIR recorded spectrum is given in Fig.3. Based on the chemical structure of KAP and boric acid the frequency assignment have been made to establish the functional groups present in the grown crystal. The FTIR spectra reveal that the KAP crystal has undergone considerable lattice distortion. In the FTIR spectrum of pure KAP crystals, the O-H symmetrical stretching observed at 3650 cm^{-1} whereas it appeared at 3651 cm^{-1} for boric acid doped KAP. Aromatic stretching (C-H) appeared in the frequency range 2478 cm^{-1} for pure KAP, but it was shifted to 2485 cm^{-1} for BKAP. C-O stretching vibrations appear at 1153 cm- and 1146 cm^{-1} for pure KAP and BKAP respectively. C=C ring stretching vibration exists at 1483 cm^{-1} and 1485 cm^{-1} for pure KAP and boric acid doped KAP respectively. The C-H out of plane bending bands was observed at 1946 cm^{-1} and 854$cm^{-1}$for boric acid doped KAP. The variation in the FTIR spectrum for the doped crystals is due to the incorporation of metal ion. The vibrational assignments for the pure and doped KAP crystals are given in Table.2.

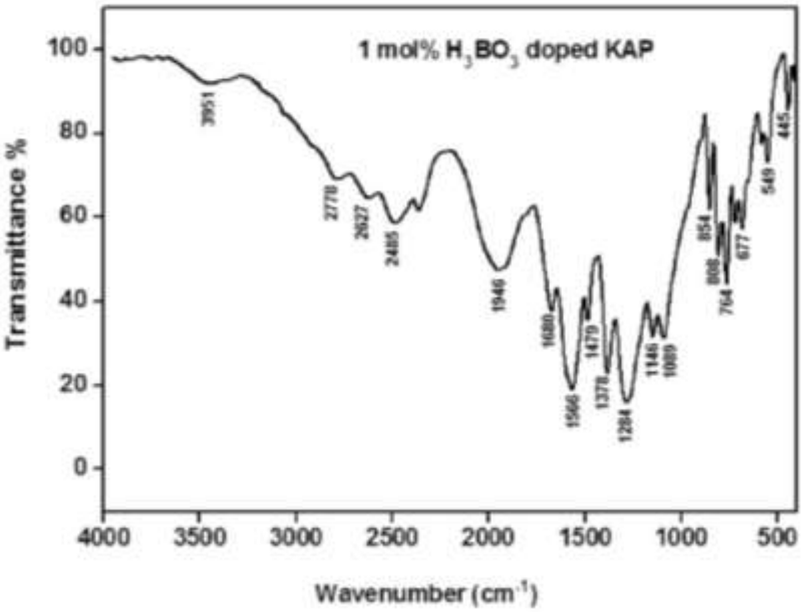

Fig.3: FTIR spectrum of the grown crystal

Table.2: Observed and Calculated IR frequencies of doped crystal

Observed IR frequencies		**Assignments**
Pure KAP [21]	**1mole% boric acid + KAP**	
3650	3651	O-H Symmetrical stretching
2478	2485	C-H Aromatic Stretching
1949	1946	C-H out of plane bending
1562	1566	C=O Carboxylate Ion O=asymmetric stretching
1485	1479	C=C ring stretching
1284	1284	C=O carboxylate ion O symmetric stretching
1153	1146	C-C stretching
848	854	C-H out of plane bending
762	764	C-C stretching

3.3UV-Vis spectral studies

The optical properties of a material are important, as they provide information on the band structure localized state and types of optical transitions. The UV-Visible transmission spectrum was recorded using Perkin Elmer Model-Lambda 35 spectrometer in the range 200 - 800 nm. From the spectrum of Fig.4. It is observed that the boric acid doped KAP crystals show little absorbance in the entire visible region. The addition of boric acid seems to have increased the crystalline perfection in KAP thereby resulting in lesser absorbance. The cut off wavelength is around 318 nm for BKAP crystals also pure KAP around 300 nm. The UV-Vis data reveals that boric acid additives improve the optical transparency of the crystal and confirm the betterment of optical quality.

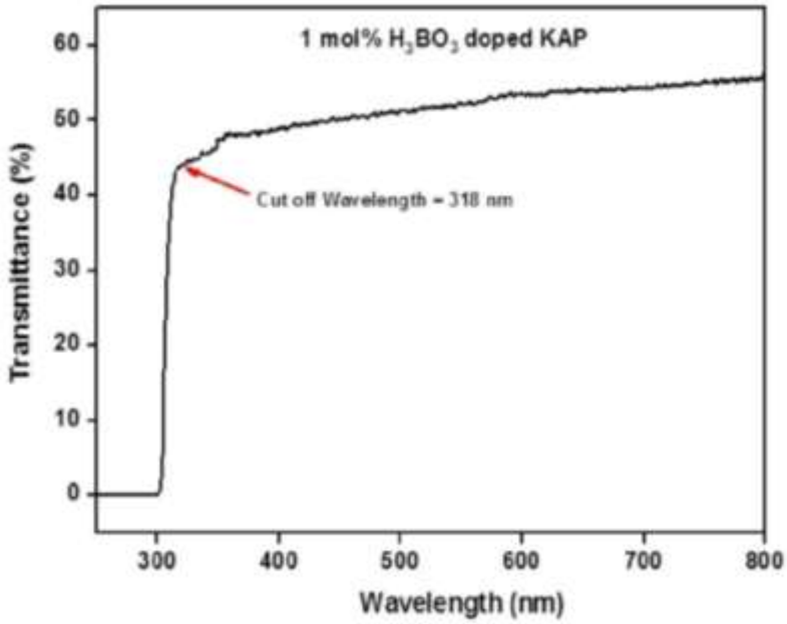

Fig.4: UV-Vis Spectrum of boric acid doped KAP

3.4 Micro hardness studies

Hardness test is useful to find the mechanical hardness of the crystal and to estimate the threshold mechanical stress. Vickers hardness measurement of boric acid doped KAP crystals were noted by applying loads of 25g, 50g, and 100g for an indentation time of 7 seconds, for each trial. Repeated trials were performed to ascertain the correctness of the observed results. The Vicker's microhardness number (Hv) was calculated using the relation,

$Hv = 1.8544\ P/d^2\ (Kg/mm^2)$

Where P is the indenter load in Kg and d is the diagonal length of the impression in mm. The plot of Vicker's hardness number versus load was shown in Fig.5.

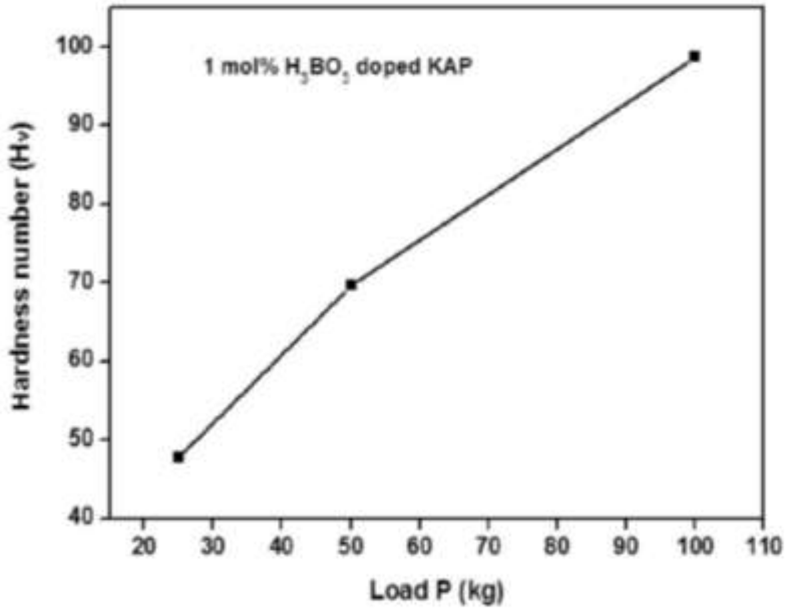

Fig.5: Plot of P vs. H_v

At slightly higher loads significant cracking occurs, which may be due to the release of internal stress generated by indentation. From the Fig.6.It is seen that the work hardness number of the BKAP crystal is 4.38. The addition of boric acid increases the hardness of the crystal. This is because of the incorporation of the boron ions into superficial crystal lattice and removing defect centers which reduce the weak lattice stresses on the surface [7].

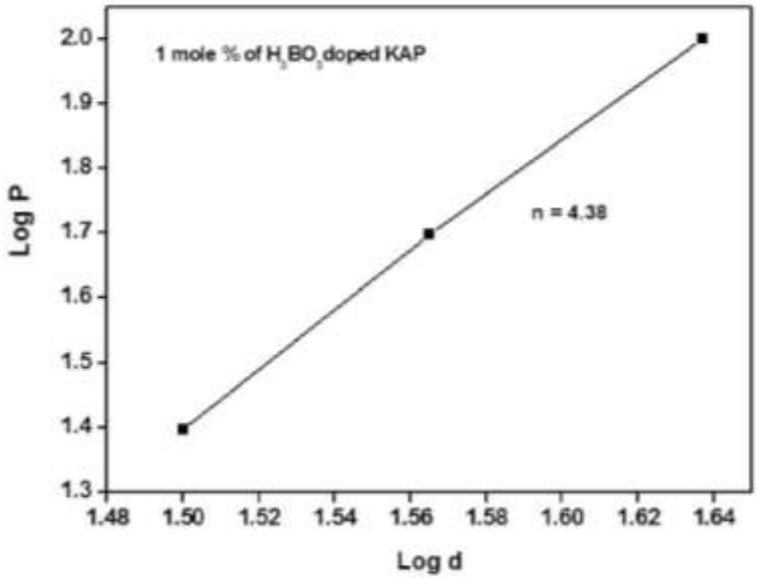

Fig.6: Plot of Log d vs. log P

3.5Thermal Analysis (DSC)

The DSC analysis of crystal grown from boric acid doped KAP solution was carried out between 0 and 350°C in the nitrogen atmosphere.DSC analysis clearly shows that there is no physically adsorbed water in the molecular structure of crystals grown. Fig.7. shows that the melting point of the boric acid doped crystal is 298.5°C. The compound is stable and there is no phase transition till it is melting. No decomposition up the melting point ensures the suitability of the material for application in lasers where the crystals are required to withstand high temperatures. It is interesting to observe that the small quantity addition of doped materials makes the crystal melts at a higher temperature (298.5°C) than the pure KAP (250°C) [8] implying enhanced mechanical stability. It roughly suggests that there is some interaction between the host crystal and the dopant.

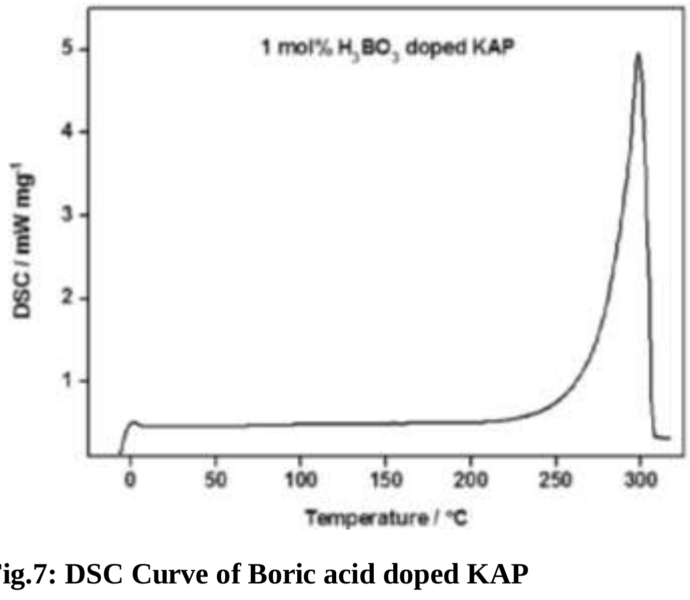

Fig.7: DSC Curve of Boric acid doped KAP

3.6 SHG Efficiency

The Kurtz and Perry powder technique remains an extremely valuable tool for initial screening of materials for second harmonic generation. The fundamental beam 1064 nm from Q-switched Nd: YAG laser was used to test SHG property of the boric acid doped KAP crystals using Kurtz powder technique. Pulse energy of 4 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz was used. The fundamental beam was filtered using an IR filter and a photomultiplier tube was used as a detector. KDP was used as the reference material and it was found that the SHG powder output was 0.52 times higher than that of KDP.

4. Conclusions

Optical quality, colorless and transparent single crystals of pure and 1 mole% boric acid added KAP were grown employing slow evaporation solution growth technique. Single crystal X-ray diffraction studies reveal that the boric acid doped KAP belongs to orthorhombiccrystal system. The FTIR spectral studies confirm the presence of all the functional groups and also presence of boric acid in the grown crystal. The optical transmission in the entire visible region for the boric acid doped KAP crystal. DSC analysis reveals that there is no decomposition upto 298.5°C and reveals the suitability of the material for laser applications. The work hardening number of boric acid doped KAP crystal is 4.38. Hence the mechanical stability of the crystals has been studied using Vickers hardness testing. The SHG efficiency of boric acid doped KAP is 0.52 times greater than that of pure KDP. This result indicates that the grown crystals are useful for NLO device application and the moderate SHG efficiency make boric acid doped KAP a potential candidate material for photonics device fabrication.

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